



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 920 967 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.06.1999 Bulletin 1999/23

(51) Int. Cl.⁶: B29C 43/08, B29C 43/36,
B29C 43/18, B65D 51/00,
A61J 1/00

(21) Application number: 98122045.2

(22) Date of filing: 20.11.1998

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 05.12.1997 US 985955

(71) Applicant:

Becton, Dickinson and Company
Franklin Lakes, New Jersey 07417-1880 (US)

(72) Inventors:

• Hwang, Chorng-Fure Robin
Cary, North Carolina 27513 (US)

• Martin, Frank E.
Durham, North Carolina 27704 (US)
• Sullivan, Tim M.
Cary, North Carolina 27513 (US)
• Williams, Joel L.
Cary, NC 27511 (US)

(74) Representative:

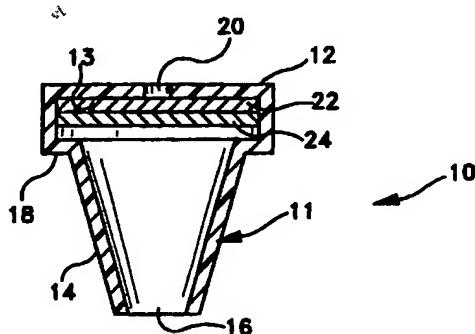
von Kreisler, Alek, Dipl.-Chem. et al
Patentanwälte,
von Kreisler-Selting-Werner,
Bahnhofsvorplatz 1 (Deichmannhaus)
50667 Köln (DE)

(54) Process for manufacture of closure assembly

(57) A process for making a closure assembly includes placing a closure cap portion in a compression mold, introducing a melt of elastomer, pressing the melt into a septum against the cap and applying a foil barrier

against the septum. The process may be performed in a rotary compression molding apparatus.

FIG-2



EP 0 920 967 A1

Description

[0001] 1. **Field of Invention:** This invention relates to molding processes, and more particularly relates to an improved process by which multi-component closures may be molded by an operationally simple and cost efficient process.

[0002] 2. **Background of the Invention:** Multi-component closures for vessels such as flasks, vials, tubes and the like have conventionally been manufactured by injection or compression molding of the individual components and subsequently combining the individual parts in one or more separate processes. For example, in the manufacture of tube closures, a septum for penetration by a needle is stamped out of an elastomeric sheet and adhered to a performed cap portion. Additional components, such as a foil lining, may then be added.

[0003] Such processes are inefficient from a processing standpoint and also result in material waste at each step. In all injection molding machines, some polymer remains in the sprue after the mold is closed, leaving a projecting piece or tab which must be removed after the product is ejected from the mold. Often, the tabs are simply discarded, or for reasons of economy, may be recovered and recycled. In either case the inefficiency and additional cost which result lead to reduced productivity from the mold.

[0004] In compression molding, an apparatus which resembles a waffle iron is used wherein melted polymer fills all mold cavities without passing through gates and runners. When all the cavities are filled, the mold is closed and heat and pressure are applied from a hydraulic press. While this process eliminates gates and runners, a surplus of polymer must be used to ensure total cavity fill. The heat and pressure cause the polymer to fill the cavity and cause spillage out into overflow grooves. Polymer in the grooves, like the tabs in injection molding, must be recycled or discarded. Compression molding, like injection molding, is inherently a batch process but is less efficient than injection molding, because a separate machine is required to separate the individual articles from the single large "Waffle" which comes out of the compression mold.

[0005] Rotary compression molding is a recent development in which individual molds on the track of a continuously revolving platform are individually charged with a melt of thermoplastic material. Compression and heating of the thermoplastic in the mold by a plunger forms the desired article. The mold-plunger unit advances along the track and is opened when the article has solidified.

SUMMARY OF THE INVENTION

[0006] In a process for making a closure assembly, a closure cap having an open lower end and a top wall having an opening is placed, top wall down, in a com-

pression mold. A predetermined quantity of a thermoplastic elastomer (TPE) is added to the cap and pressed by a matching male forming pin into a septum which covers the opening and adheres to the underside of the top wall. A permeability lowering barrier may then be pressed against the septum. In a preferred process, the cap is introduced to the female cavity of a compression mold at a first station of a rotary compression molding apparatus and subsequent steps of the process are performed sequentially at later stations.

[0007] Conventional processes for making closure assemblies include preparing a performed sheet of elastomeric material, laminating a foil barrier material thereto, stamping septum-foil units from the laminated sheet and adhering these to injection molded caps, often with an adhesive. These procedures are time consuming and up to 30% of the elastomer is lost during the stamping operation and must be discarded or recycled. The present invention overcomes the lost time and material of conventional processes, eliminates any need for adhesive, and is accordingly much more efficient.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

Fig 1 is a perspective view of a closure assembly made by the process of the invention;

Fig 2 is a vertical sectional view of the assembly of Fig 1 taken along the line 2-2 thereof; and

Fig 3 is a top plan view of the assembly of Fig 1.

DETAILED DESCRIPTION

[0009] While this invention is satisfied by embodiments in many different forms, there will herein be described in detail embodiments of the invention with the understanding that the present disclosure is to be considered as exemplary of the principles of the invention and is not intended to limit the invention to the embodiments illustrated and described. The scope of the invention will be measured by the appended claims and their equivalents.

[0010] In the process of the invention, a multi-component closure assembly is produced by compression molding a puncturable septum directly across an opening in a cap portion, and then, without removing the cap-septum unit from the mold, a permeability-lowering barrier is introduced and adhered to the septum.

[0011] Adverting now to the drawings, Figs 1-3 illustrate a typical tube closure assembly fabricated by the process of the invention. Assembly 10 includes a cap portion 11 having an annular top wall 12 having a bottom edge 13 and a side wall 14 defining an open bottom end 16. Side wall 14 may include a shelf 18 for engage-

ment with the lip of a tube (not shown). Top wall 12 includes an opening 20 to receive a needle. A septum 22 is adjacent and adhered to bottom edge 13 of cap portion 11. A permeability lowering barrier 24 is adjacent and adhered to septum 22. As shown in Fig 3, septum 22 is visible through opening 20 when the closure assembly is viewed from above.

[0012] The cap portion 11 of the assembly may be fabricated by any conventional process, such as injection molding, and may be of any conventional plastic which is compatible with and forms a secure bond with the material selected for the septum, as delineated below. Preferred plastics for the cap are polyolefins, such as polyethylene or polypropylene, polyethylene terephthalate (PET) and polystyrene. Fabrication of the cap portion is not part of this invention. The injection molded cap portion may be placed in the female cavity of a compression mold with top wall 12 in the bottom of the cavity so that open bottom end 16 faces up. A quantity of melt of TPE predetermined to form septum 22 is then introduced, preferably by extrusion, into the cap portion in the mold cavity. A matching male forming pin is introduced into the female cavity to force the elastomer into the shape of septum 22 which is thereby pressed against and bonds with bottom edge 13 of cap top wall 12.

[0013] Any TPE which forms a secure bond to the cap may be used for the septum. Suitable thermoplastics for septums to be used with polystyrene caps are for example acrylonitrile- butadiene-styrene or styrene-butadiene rubbers. For PET caps a septum of polyester TPE, such as HYTREL™ (DuPont) is preferred.

[0014] Elastomers suitable for septums to be used with polyolefin caps are thermoplastic polyolefin rubbers, generally referred to as TPOs, for example ethylene-propylene-diene monomer (EPDM) rubber in a polypropylene matrix, commercially available under the trade name SANTOPRENE™ from AES (Advanced Elastomer Systems, Akron, Ohio).

[0015] A preferred elastomer for septums to be used with polyolefin caps is the class of copolymers known in the art as metallocene copolyolefins, i.e., copolymers made using metallocene catalysts. Exemplary of such products are copolymers of ethylene with an alpha olefin of 3-20 carbon atoms. These products are commercially available from Exxon under the trade name EXACT™ or from Dow under the trade name ENGAGE™.

[0016] The most preferred elastomer for a septum to be used with a polyolefin cap is a metallocene copolymer of the EXACT or ENGAGE series which has been silane-grafted to contain about 0.2-10% by weight of silane. Silane-grafted metallocene polyolefin copolymers are well known in the art and are fully described in European Patent Application EP 0 702 032A2 and International Application No. WO 95/29197. They form exceptionally strong bonds to polyolefin caps. Silanes which may be grafted to polyolefins are sold by HULS

AG (Somerset, N.J.) under the trade name DYNASY-LAN™. A preferred grafting agent is vinyl trimethoxy silane.

[0017] If it is desired that the septum be hardened, the cap-septum unit in the mold may optionally be exposed to moisture to crosslink the polymer of the septum through siloxane groups. Crosslinking of silane-grafted metallocene polyolefins is conventional in the art.

[0018] Without removing the cap-septum unit from the mold, a permeability lowering barrier may be pressed against and bonded to the septum. The barrier preferably is of foil, most preferably aluminum foil, though any other suitable material as known in the art may be used. If a more secure bond between the septum and the foil barrier is desired, the foil may be coated with any suitable adhesive such as CHEMLOK™ (Lord Corporation, Erie, PA). The barrier may be about 0.3 to 3 micron thick.

[0019] The preferred process of the invention is continuous. In this embodiment of the invention, a line of female compression molds moves along a track. Each mold visits sequentially a series of stations where an operation in the process takes place. Thus, at a first station along the track, the mold receives the injection molded cap portion, as described above. The mold containing the cap advances along the track to a second station where the predetermined quantity of elastomer is extruded into the cap in the mold. At this station, the mating male forming pin may be introduced to compression mold the elastomer into the shape of the septum, or preferably, the mold, after receiving the elastomer, may be advanced to the next sequential station where the forming pin enters the mold and compression molds the elastomer into the septum and against the bottom edge of the top wall of the cap. The forming pin may then be retracted and the foil or foil-adhesive unit introduced and pressed against the septum by reentry of the forming pin.

[0020] Alternatively, the mold containing the cap-septum unit may be further advanced and the foil barrier introduced at a subsequent station. An apparatus suitable for the continuous process of the invention is described in detail in U.S. Patent No. 4,314,799.

[0021] In any closure, it is critical that the septum bond securely to the cap so that no separation or leakage occurs. For example, it is readily seen that failure of the septum-cap seal would compromise the vacuum in an evacuated blood collection tube and lead to incomplete sample collection. In the present invention, it has been found that compression molding the melt bonds the elastomeric septum against the cap with sufficient strength so that adhesive is not required and leakage does not occur. Bond strength between septum and cap in closures made by the process of the invention and the prior art may be tested qualitatively for leakage by the procedure of the Example.

EXAMPLE

[0022] The closure to be tested for leakage was inserted into the open end of a 16X100 mm plastic tube. Ten ml of water were added (80% fill), and the tube was dropped from heights of 78 and 39 in. onto a laboratory floor (simulated hospital floor). The tubes were then visually examined for leakage through the cap-septum seal. No separation of septum from cap was observed with the following closure assemblies made by the process of the invention, and no leakage was observed.

- 1) polystyrene cap - HYTREL septum-foil barrier
- 2) polypropylene cap - SANTOPRENE septum-foil barrier
- 3) polypropylene cap - silane-grafted EXACT septum-foil barrier

Claims

1. A process for making a closure assembly comprising:
 - a) placing a plastic cap portion of a closure assembly having a top wall defining an opening into the female cavity of a compression mold, said cap portion being placed with said top wall adjacent to the bottom wall of said mold;
 - b) adding a thermoplastic elastomer to said cap portion;
 - c) pressing said elastomer into a septum sealed against said top wall and covering said opening; and
 - d) affixing a permeability lowering barrier to said septum.
2. The process of Claim 1 wherein said elastomer is pressed into said septum by a matching male forming pin.
3. The process of Claim 2 wherein said cap portion is placed in the female cavity of a compression mold at a first station of a rotary compression molding apparatus.
4. The process of Claim 1 wherein said plastic cap is of polystyrene, polyolefin or polyethylene terephthalate.
5. The process of Claim 1 wherein said elastomer is selected from a group consisting of styrene-butadiene rubber, ethylene propylene diene monomer rubber, a copolymer of ethylene and an alpha olefin of 3-20 carbon atoms, and a silane grafted copolymer of ethylene and an alpha olefin of 3-20 carbon atoms.
6. A process for making a closure assembly comprising:
 - a) placing a polyolefin cap portion of a closure assembly having a top wall defining an opening into the female cavity of a compression mold, said top wall being adjacent to the bottom wall of said mold;
 - b) introducing a melt of a copolymer of ethylene and an alpha olefin of 3-20 carbon atoms into said cap portion;
 - c) pressing said copolymer with a matching male pin to form a septum against said top wall and covering said opening; and
 - d) affixing a permeability-lowering barrier to said septum.
7. The process of Claim 6 wherein said copolymer includes sane grafts.
8. The process of Claim 7 further comprising crosslinking said septum of silane-grafted copolymer.
9. A process for making a tube closure assembly comprising:
 - a) placing a polyolefin cap portion of a closure assembly having a top wall defining an opening into the female cavity of a compression mold at a first station of a rotary compression molding apparatus, the top wall of said cap portion being placed adjacent to the bottom of said mold;
 - b) adding a predetermined quantity of a melt of a silane-grafted copolymer of ethylene and an alpha olefin of 3-20 carbon atoms into said cap portion in said female cavity;
 - c) pressing said copolymer with a matching male pin to form a septum against said top wall and covering said opening; and
 - d) pressing a permeability-lowering barrier against said septum with said male pin.
10. The process of Claim 9 wherein the septum is crosslinked.

ing:

FIG-1

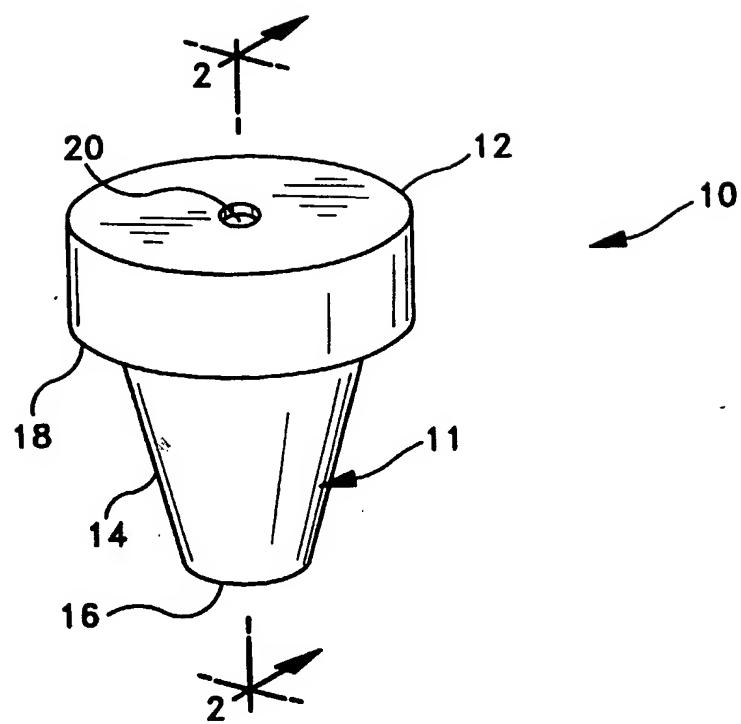


FIG-2

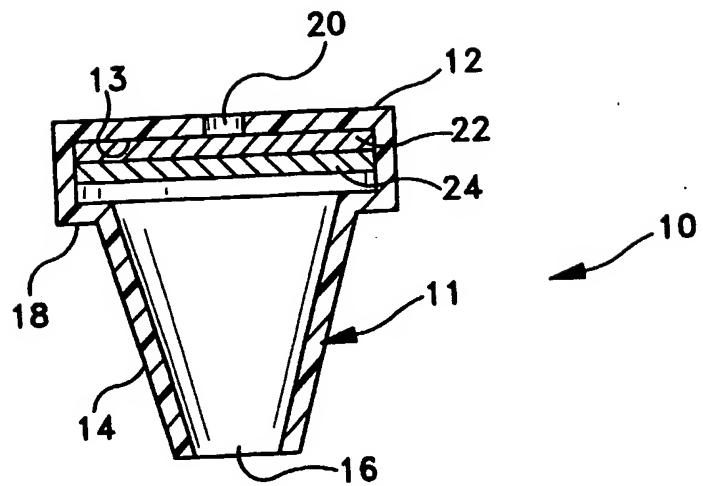
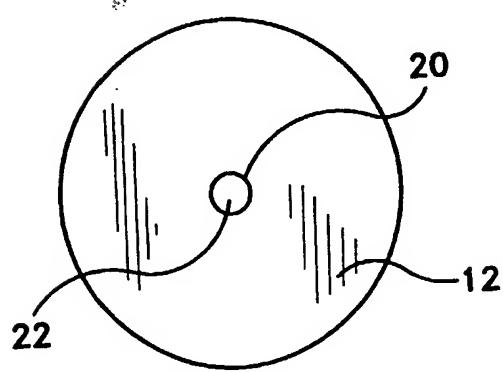


FIG-3





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 12 2045

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US 5 647 939 A (GEE ALAN R ET AL) 15 July 1997 * column 3, line 1 - line 15 * * example 1 * ---	1,4-7	B29C43/08 B29C43/36 B29C43/18 B65D51/00 A61J1/00
A	FR 2 618 683 A (AGUETTANT LAB) 3 February 1989 * page 4, line 3 - page 6, line 13 * * claims 1,2,7 * ---	1,3-6	
A	US 4 497 765 A (MCCANDLESS THOMAS J ET AL) 5 February 1985 * column 5, line 63 * * figure 3D * * column 3, line 3 * * column 9, line 52 - line 27 * -----	1,4,6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B29C B65D A61J
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search		Examiner
MUNICH	15 March 1999		Philpott, G
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-written disclosure P : intermediate document			

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 98 12 2045

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-03-1999

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5647939 A	15-07-1997	AU	4414996 A	03-07-1996
		EP	0797529 A	01-10-1997
		JP	10500637 T	20-01-1998
		WO	9618550 A	20-06-1996
FR 2618683 A	03-02-1989	NONE		
US 4497765 A	05-02-1985	US	4343754 A	10-08-1982
		AU	560751 B	16-04-1987
		AU	8555282 A	27-01-1983
		BR	8204327 A	19-07-1983
		CA	1215206 A	16-12-1986
		CA	1289104 A	17-09-1991
		DE	3277686 A	23-12-1987
		EP	0073334 A	09-03-1983
		GB	2108892 A,B	25-05-1983
		AU	540432 B	15-11-1984
		AU	6339280 A	14-04-1981
		BR	8008834 A	30-06-1981
		CA	1168812 A	12-06-1984
		EP	0026405 A	08-04-1981
		JP	56501121 T	13-08-1981
		JP	63048704 B	30-09-1988
		WO	8100822 A	02-04-1981



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 920 967 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
13.02.2002 Bulletin 2002/07

(51) Int Cl.7: **B29C 43/08, B29C 43/36,**
B29C 43/18, B65D 51/00,
A61J 1/00

(21) Application number: 98122045.2

(22) Date of filing: 20.11.1998

(54) Process for manufacture of closure assembly

Verfahren zur Herstellung von einer Verschlusseinheit

Procédé pour la fabrication d'un dispositif de fermeture

(84) Designated Contracting States:
DE FR GB IT

- **Sullivan, Tim M.**
New Freedom, PA 17349 (US)
- **Williams, Joel L.**
Cary, NC 27511 (US)

(30) Priority: 05.12.1997 US 985955

(43) Date of publication of application:
09.06.1999 Bulletin 1999/23

(74) Representative:
von Kreisler, Alek, Dipl.-Chem. et al
Patentanwälte, von Kreisler-Selting-Werner,
Bahnhofsvorplatz 1 (Deichmannhaus)
50667 Köln (DE)

(73) Proprietor: Becton, Dickinson and Company
Franklin Lakes, New Jersey 07417-1880 (US)

(72) Inventors:

- Hwang, Chorng-Fure Robin
Cary, North Carolina 27513 (US)
- Martin, Frank E.
Durham, North Carolina 27704 (US)

EP 0 9920 9967 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] Field of Invention: This invention relates to molding processes, and more particularly relates to an improved process by which multi-component closures may be molded by an operationally simple and cost efficient process.

[0002] Background of the Invention: Multi-component closures for vessels such as flasks, vials, tubes and the like have conventionally been manufactured by injection or compression molding of the individual components and subsequently combining the individual parts in one or more separate processes. For example, in the manufacture of tube closures, a septum for penetration by a needle is stamped out of an elastomeric sheet and adhered to a performed cap portion. Additional components, such as a foil lining, may then be added.

[0003] Such processes are inefficient from a processing standpoint and also result in material waste at each step. In all injection molding machines, some polymer remains in the sprue after the mold is closed, leaving a projecting piece or tab which must be removed after the product is ejected from the mold. Often, the tabs are simply discarded, or for reasons of economy, may be recovered and recycled. In either case the inefficiency and additional cost which result lead to reduced productivity from the mold.

[0004] In compression molding, an apparatus which resembles a waffle iron is used wherein melted polymer fills all mold cavities without passing through gates and runners. When all the cavities are filled, the mold is closed and heat and pressure are applied from a hydraulic press. While this process eliminates gates and runners, a surplus of polymer must be used to ensure total cavity fill. The heat and pressure cause the polymer to fill the cavity and cause spillage out into overflow grooves. Polymer in the grooves, like the tabs in injection molding, must be recycled or discarded. Compression molding, like injection molding, is inherently a batch process but is less efficient than injection molding, because a separate machine is required to separate the individual articles from the single large "waffle" which comes out of the compression mold.

[0005] Rotary compression molding is a recent development in which individual molds on the track of a continuously revolving platform are individually charged with a melt of thermoplastic material. Compression and heating of the thermoplastic in the mold by a plunger forms the desired article. The mold-plunger unit advances along the track and is opened when the article has solidified.

[0006] US-A-5647939 discloses a method of making an open top cap in which a silicone rubber septum is directly bonded to the flange of an open top plastic cap by separately ionizing a surface of the elastomer and ionizing a surface of the plastic and then immediately compressing the ionized surfaces together while applying pressure and heat.

SUMMARY OF THE INVENTION

[0007] In a process for making a closure assembly, a closure cap having an open lower end and a top wall 5 having an opening is placed, top wall down, in a compression mold. A predetermined quantity of a thermoplastic elastomer (TPE) is added to the cap and pressed by a matching male forming pin into a septum which covers the opening and adheres to the underside of the top wall. A permeability lowering barrier may then be pressed against the septum. In a preferred process, the cap is introduced to the female cavity of a compression mold at a first station of a rotary compression molding apparatus and subsequent steps of the process are performed sequentially at later stations.

[0008] Conventional processes for making closure assemblies include preparing a performed sheet of elastomeric material, laminating a foil barrier material thereto, stamping septum-foil units from the laminated sheet 20 and adhering these to injection molded caps, often with an adhesive. These procedures are time consuming and up to 30% of the elastomer is lost during the stamping operation and must be discarded or recycled. The present invention overcomes the lost time and material of conventional processes, eliminates any need for adhesive, and is accordingly much more efficient.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig 1 is a perspective view of a closure assembly made by the process of the invention;

[0010] Fig 2 is a vertical sectional view of the assembly of Fig 1 taken along the line 2-2 thereof; and

Fig 3 is a top plan view of the assembly of Fig 1.

DETAILED DESCRIPTION

[0010] In particular, the present invention relates to a process for making a closure assembly (10) comprising the sequential steps of:

- 45** a) placing a plastic cap portion (11) of a closure assembly (10) having a top wall (12) defining an opening (20) into the female cavity of a compression mold, said cap portion being placed with said top wall (12) adjacent to the bottom wall (16) of said mold;
- 50** b) adding a thermoplastic elastomer to said cap portion (11);
- c) pressing said elastomer into a septum (22) sealed against said top wall (12) and covering said opening (20); and
- 55** d) affixing a permeability lowering barrier (24) to said septum (22).

Preferred embodiments become evident from the dependent claims.

[0011] In the process of the invention, a multi-component closure assembly is produced by compression molding a puncturable septum directly across an opening in a cap portion, and then, without removing the cap-septum unit from the mold, a permeability-lowering barrier is introduced and adhered to the septum.

[0012] Referring now to the drawings, Figs 1-3 illustrate a typical tube closure assembly fabricated by the process of the invention. Assembly 10 includes a cap portion 11 having an annular top wall 12 having a bottom edge 13 and a side wall 14 defining an open bottom end 16. Side wall 14 may include a shelf 18 for engagement with the lip of a tube (not shown). Top wall 12 includes an opening 20 to receive a needle. A septum 22 is adjacent and adhered to bottom edge 13 of cap portion 11. A permeability lowering barrier 24 is adjacent and adhered to septum 22. As shown in Fig 3, septum 22 is visible through opening 20 when the closure assembly is viewed from above.

[0013] The cap portion 11 of the assembly may be fabricated by any conventional process, such as injection molding, and may be of any conventional plastic which is compatible with and forms a secure bond with the material selected for the septum, as delineated below. Preferred plastics for the cap are polyolefins, such as polyethylene or polypropylene, polyethylene terephthalate (PET) and polystyrene. Fabrication of the cap portion is not part of this invention. The injection molded cap portion may be placed in the female cavity of a compression mold with top wall 12 in the bottom of the cavity so that open bottom end 16 faces up. A quantity of melt of TPE predetermined to form septum 22 is then introduced, preferably by extrusion, into the cap portion in the mold cavity. A matching male forming pin is introduced into the female cavity to force the elastomer into the shape of septum 22 which is thereby pressed against and bonds with bottom edge 13 of cap top wall 12.

[0014] Any TPE which forms a secure bond to the cap may be used for the septum. Suitable thermoplastics for septums to be used with polystyrene caps are for example acrylonitrile- butadiene-styrene or styrene-butadiene rubbers. For PET caps a septum of polyester TPE, such as HYTREL™ (DuPont) is preferred.

[0015] Elastomers suitable for septums to be used with polyolefin caps are thermoplastic polyolefin rubbers, generally referred to as TPOs, for example ethylene-propylene-diene monomer (EPDM) rubber in a polypropylene matrix, commercially available under the trade name SANTOPRENE™ from AES (Advanced Elastomer Systems, Akron, Ohio).

[0016] A preferred elastomer for septums to be used with polyolefin caps is the class of copolymers known in the art as metallocene copolyolefins, i.e., copolymers made using metallocene catalysts. Exemplary of such products are copolymers of ethylene with an alpha olefin

of 3-20 carbon atoms. These products are commercially available from Exxon under the trade name EXACT™ or from Dow under the trade name ENGAGE™.

[0017] The most preferred elastomer for a septum to be used with a polyolefin cap is a metallocene copolymer of the EXACT or ENGAGE series which has been silane-grafted to contain about 0.2-10% by weight of silane. Silane-grafted metallocene polyolefin copolymers are well known in the art and are fully described in European Patent Application EP 0 702 032A2 and International Application No. WO 95/29197. They form exceptionally strong bonds to polyolefin caps. Silanes which may be grafted to polyolefins are sold by HULS AG (Somerset, N.J.) under the trade name DYNASYLAN™. A preferred grafting agent is vinyl trimethoxy silane.

[0018] If it is desired that the septum be hardened, the cap-septum unit in the mold may optionally be exposed to moisture to crosslink the polymer of the septum through siloxane groups. Crosslinking of silane-grafted metallocene polyolefins is conventional in the art.

[0019] Without removing the cap-septum unit from the mold, a permeability lowering barrier is pressed against and bonded to the septum. The barrier preferably is of foil, most preferably aluminum foil, though any other suitable material as known in the art may be used. If a more secure bond between the septum and the foil barrier is desired, the foil may be coated with any suitable adhesive such as CHEMLOK™ (Lord Corporation, Erie, PA). The barrier may be about 0.3 to 3 micrometers thick.

[0020] The preferred process of the invention is continuous. In this embodiment of the invention, a line of female compression molds moves along a track. Each mold visits sequentially a series of stations where an operation in the process takes place. Thus, at a first station along the track, the mold receives the injection molded cap portion, as described above. The mold containing the cap advances along the track to a second station where the predetermined quantity of elastomer is extruded into the cap in the mold. At this station, the mating male forming pin may be introduced to compression mold the elastomer into the shape of the septum, or preferably, the mold, after receiving the elastomer, may be advanced to the next sequential station where the forming pin enters the mold and compression molds the elastomer into the septum and against the bottom edge of the top wall of the cap. The forming pin may then be retracted and the foil or foil-adhesive unit introduced and pressed against the septum by reentry of the forming pin.

[0021] Alternatively, the mold containing the cap-septum unit may be further advanced and the foil barrier introduced at a subsequent station. An apparatus suitable for the continuous process of the invention is described in detail in U.S.-A-4,314,799.

[0022] In any closure, it is critical that the septum bond securely to the cap so that no separation or leakage occurs. For example, it is readily seen that failure of the

septum-cap seal would compromise the vacuum in an evacuated blood collection tube and lead to incomplete sample collection. In the present invention, it has been found that compression molding the melt bonds the elastomeric septum against the cap with sufficient strength so that adhesive is not required and leakage does not occur. Bond strength between septum and cap in closures made by the process of the invention and the prior art may be tested qualitatively for leakage by the procedure of the Example.

10

EXAMPLE

[0023] The closure to be tested for leakage was inserted into the open end of a 16X100 mm plastic tube. Ten ml of water were added (80% fill), and the tube was dropped from heights of 198.12 and 99.06 cm (78 and 39 in.) onto a laboratory floor (simulated hospital floor). The tubes were then visually examined for leakage through the cap-septum seal. No separation of septum from cap was observed with the following closure assemblies made by the process of the invention, and no leakage was observed.

15

- 1) polystyrene cap - HYTREL septum-foil barrier
- 2) polypropylene cap - SANTOPRENE septum-foil barrier
- 3) polypropylene cap - silane-grafted EXACT septum-foil barrier

20

Claims

1. A process for making a closure assembly (10) comprising the sequential steps of:

25

- a) placing a plastic cap portion (11) of a closure assembly (10) having a top wall (12) defining an opening (20) into the female cavity of a compression mold, said cap portion being placed with said top wall (12) adjacent to the bottom wall (16) of said mold;
- b) adding a thermoplastic elastomer to said cap portion (11);
- c) pressing said elastomer into a septum (22) sealed against said top wall (12) and covering said opening (20); and
- d) affixing a permeability lowering barrier (24) to said septum (22).

30

2. The process of claim 1 wherein said elastomer is pressed into said septum (22) by a matching male forming pin.

35

3. The process of claim 2 wherein said cap portion (11) is placed in the female cavity of a compression mold at a first station of a rotary compression molding apparatus.

40

4. The process of claim 1 wherein said plastic cap (11) is of polystyrene, polyolefin or polyethylene terephthalate.

5

5. The process of claim 1 wherein said elastomer is selected from a group consisting of styrene-butadiene rubber, ethylene propylene diene monomer rubber, a copolymer of ethylene and an alpha olefin of 3 - 20 carbon atoms, and a silane grafted copolymer of ethylene and an alpha olefin of 3 - 20 carbon atoms.

6

6. The process of claim 1 comprising:

- a) placing the polyolefin cap portion (11) of the closure assembly (10) having the top wall (12) defining the opening (20) into the female cavity of the compression mold, said top wall (12) being adjacent to the bottom wall (16) of said mold;
- b) introducing a melt of a copolymer of ethylene and an alpha olefin of 3 - 20 carbon atoms into said cap portion (11);
- c) pressing said copolymer with a matching male pin to form a septum (22) against said top wall (12) and covering said opening (20); and
- d) affixing a permeability-lowering barrier (24) to said septum (22).

30

7. The process of claim 6 wherein said copolymer includes silane grafts.

35

8. The process of claim 7 further comprising crosslinking said septum of silane-grafted copolymer.

45

9. The process of claim 1 comprising:

- a) placing the polyolefin cap portion (11) of the closure assembly (10) having the top wall (12) defining the opening (20) into the female cavity of the compression mold at a first station of a rotary compression molding apparatus, the top wall (12) of said cap portion being placed adjacent to the bottom of said mold;
- b) adding a predetermined quantity of a melt of a silane-grafted copolymer of ethylene and an alpha olefin of 3 - 20 carbon atoms into said cap portion (11) in said female cavity;
- c) pressing said copolymer with a matching male pin to form a septum (22) against said top wall (12) and covering said opening (20); and
- d) pressing a permeability-lowering barrier (24) against said septum with said male pin.

50

55 10. The process of claim 9 wherein the septum (22) is crosslinked.

Patentanprüch

1. Verfahren zur Herstellung einer Verschlussvorrichtung (10), umfassend die aufeinanderfolgenden Schritte des:

a) Anordnen eines Kunststoffdeckelteils (11) einer Verschlussvorrichtung (10) mit einer oberen, eine Öffnung (20) definierenden Wandung (12) im Gesenk eines Presswerkzeugs, wobei das Deckelteil so angeordnet wird, dass die obere Wandung (12) an die untere Wandung (16) des Formwerkzeugs angrenzt;

b) Eintragen eines thermoplastischen Elastomers in das Deckelteil (11);

c) Pressen des Elastomers in ein Septum (22), das gegenüber der oberen Wandung (12) abgedichtet ist und die Öffnung (20) abdeckt; und des

d) Anbringen einer durchlässigkeitssenkenden Sperrsicht (24) am Septum (22).

2. Verfahren nach Anspruch 1, wobei das Elastomer mittels eines passenden Positiv-Formgeberstifts in das Septum (22) gepresst wird.

3. Verfahren nach Anspruch 2, wobei der Deckelteil (11) im Gesenk eines Presswerkzeugs in einer ersten Station einer Rotations-Formpressvorrichtung angeordnet wird.

4. Verfahren nach Anspruch 1, wobei der Kunststoffdeckel (11) aus Polystyrol, einem Polyolefin oder Polyethylenterephthalat besteht.

5. Verfahren nach Anspruch 1, wobei das Elastomer aus der aus einem Styrol-Butadien-Kautschuk, einem Ethylen-Propylen-Dien-Monomer-Kautschuk, einem Copolymer von Ethylen und einem α -Olefin mit 3 - 20 Kohlenstoffatomen und einem silangepfropften Copolymer von Ethylen und einem α -Olefin von 3 - 20 Kohlenstoffatomen bestehenden Gruppe ausgewählt ist.

6. Verfahren nach Anspruch 1, umfassend das:

a) Anordnen eines Polyolefin-Deckelteils (11) einer Verschlussvorrichtung (10) mit einer oberen, eine Öffnung (20) definierenden Wandung (12) im Gesenk eines Presswerkzeugs, wobei die obere Wandung (12) an die untere Wandung (16) des Formwerkzeugs angrenzt;

b) Einführen einer Schmelze eines Copolymers von Ethylen und einem α -Olefin von 3 - 20 Kohlenstoffatomen in das Deckelteil (11);

c) Pressen des Copolymers mit einem passenden Positivstift, wodurch ein Septum (22) gegenüber der oberen Wandung (12) gebildet wird, wodurch die Öffnung (20) abgedeckt wird; und des

d) Anbringen einer durchlässigkeitssenkenden Sperrsicht (24) am Septum (22).

7. Verfahren nach Anspruch 6, wobei das Copolymer Silanpropfungen enthält.

8. Verfahren nach Anspruch 7, weiterhin umfassend das Vernetzen des Septums aus silangepfropftem Copolymer.

9. Verfahren nach Anspruch 1, umfassend das:

a) Anordnen des Polyolefin-Deckelteils (11) der Verschlussvorrichtung (10), deren obere Wandung (12) die Öffnung (20) definiert, im Gesenk eines Presswerkzeugs in einer ersten Station einer Rotations-Formpressvorrichtung, wobei die obere Wandung (12) des Deckelteils an die Unterseite des Formwerkzeugs angrenzt;

b) Eintragen einer vorbestimmten Menge einer Schmelze eines silangepfropften Copolymers von Ethylen und eines α -Olefins von 3 - 20 Kohlenstoffatomen in das Deckelteil (11) im Gesenk;

c) Pressen des Copolymers mittels eines passenden Positiv-Formgeberstifts, wodurch ein Septum (22) gebildet wird, das gegenüber der oberen Wandung (12) abgedichtet ist und die Öffnung (20) abdeckt; und des

d) Pressen einer durchlässigkeitssenkenden Sperrsicht (24) mittels des Positivstifts gegen das Septum.

10. Verfahren nach Anspruch 9, wobei das Septum (22) vernetzt ist.

Revendications

1. Un procédé pour la fabrication d'un dispositif de fermeture (10) comprenant les étapes séquentielles consistant à :

a) placer une partie de capuchon en matière plastique (11) d'un dispositif de fermeture (10) ayant une paroi de dessus (12) définissant une ouverture (20) dans la cavité fermelle d'un mou-

le de compression, ladite partie de capuchon étant placée avec ladite paroi de dessus (12) contiguë à la paroi de fond (16) dudit moule ;
 b) ajouter un élastomère thermoplastique à ladite partie de capuchon (11) ;
 c) appliquer ledit élastomère dans un septum (22) étanchéifié vis-à-vis de ladite paroi de dessus (12) et recouvrir ladite ouverture (20) ; et
 d) fixer une barrière abaissant la perméabilité (24) audit septum (22). 10

2. Le procédé selon la revendication 1, dans lequel ledit élastomère est appliqué dans ledit septum (22) par adaptation d'une goupille de conformation mâle. 15

3. Le procédé selon la revendication 2, dans lequel ladite partie de capuchon (11) est placée dans la cavité femelle d'un moule de compression en un premier poste d'un appareil de moulage par compression rotatif. 20

4. Le procédé selon la revendication 1, dans lequel ledit capuchon en matière plastique (11) est en polystyrène, en polyoléfine ou en polytéraphthalate d'éthylène. 25

5. Le procédé selon la revendication 1, dans lequel ledit élastomère est choisi parmi le groupe comprenant le caoutchouc styrène-butadiène, le caoutchouc monomère de diène éthylène propylène, un copolymère d'éthylène et une alpha-oléfine ayant de 3 à 20 atomes de carbone, et un copolymère d'éthylène greffé de silane et une alpha-oléfine ayant de 3 à 20 atomes de carbone. 30

6. Le procédé selon la revendication 1, comprenant les étapes consistant à: 35

a) placer la partie de capuchon de polyoléfine (11) du dispositif de fermeture (10) ayant la paroi de dessus (12) définissant l'ouverture (20) dans la cavité femelle du moule de compression, ladite paroi de dessus (12) étant contiguë à la paroi inférieure (16) dudit moule ;
 b) introduire un produit fondu d'un copolymère d'éthylène et d'une alpha-oléfine ayant de 3 à 20 atomes de carbone dans ladite partie de capuchon (11);
 c) presser ledit copolymère avec une goupille mâle d'adaptation pour former un septum (22) contre ladite paroi de dessus (12) et recouvrir ladite ouverture (20) ; et
 d) fixer une barrière abaissant la perméabilité (24) contre ledit septum avec ladite goupille mâle. 40

7. Le procédé selon la revendication 6, dans lequel ledit copolymère comprend des greffes de silane. 45

8. Le procédé selon la revendication 7, comprenant, en outre, la réticulation dudit septum du copolymère greffé de silane. 50

5 9. Le procédé selon la revendication 1, comprenant les étapes consistant à:

a) placer la partie de capuchon de polyoléfine (11) du dispositif de fermeture (10) ayant la paroi de dessus (12) définissant l'ouverture (20) dans la cavité femelle du moule de compression en un premier poste d'un appareil de moulage par compression rotatif, la paroi de dessus (12) de ladite partie de capuchon étant placée de façon contiguë au fond dudit moule ;
 b) ajouter une quantité prédéterminée d'un produit fondu d'un copolymère greffé de silane d'éthylène et d'une alpha-oléfine ayant de 3 à 20 atomes de carbone dans ladite partie de capuchon (11) dans ladite cavité femelle ;
 c) appliquer ledit copolymère avec une goupille mâle d'adaptation pour former un septum (22) contre ladite paroi de dessus (12) et recouvrir ladite ouverture (20) ; et
 d) appliquer une barrière abaissant la perméabilité (24) contre ledit septum avec ladite goupille mâle. 55

10. Le procédé selon la revendication 9, dans lequel le septum (22) est réticulé. 60

FIG-1

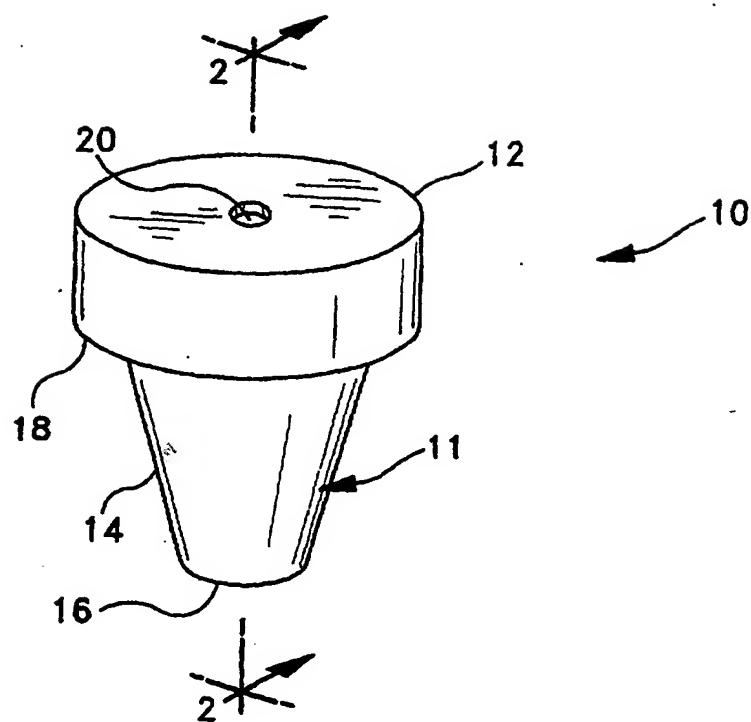


FIG-2

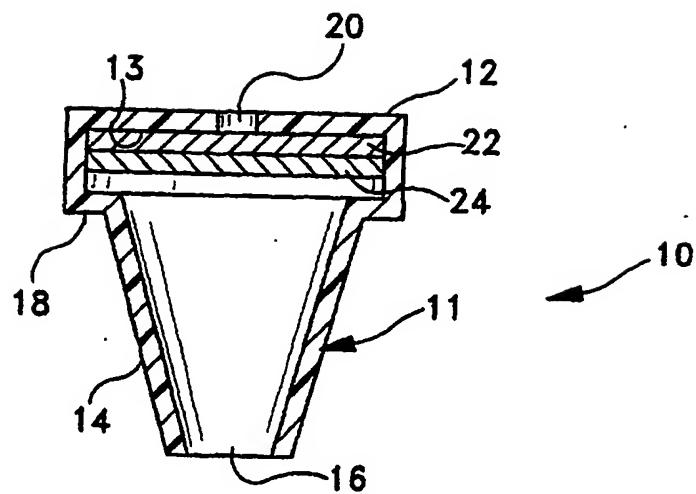


FIG-3

